

Development and Characterization of Improved NiTiPd High-Temperature Shape-Memory Alloys by Solid-Solution Strengthening and Thermomechanical Processing

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Abstract

The need for compact, solid-state actuation systems for use in the aerospace, automotive, and other transportation industries is currently motivating research in high-temperature shape-memory alloys (HTSMA) with transformation temperatures greater than 100°C. One of the basic high-temperature alloys investigated to fill this need is Ni_{19.5}Ti_{50.5}Pd₃₀. Initial testing has indicated that this alloy, while having acceptable work characteristics, suffers from significant permanent deformation (or ratcheting) during thermal cycling under load. In an effort to overcome this deficiency, various solid-solution alloying and thermomechanical processing schemes were investigated. Solid-solution strengthening was achieved by substituting 5at% gold or platinum for palladium in Ni_{19.5}Ti_{50.5}Pd₃₀, the so-called baseline alloy, to strengthen the martensite and austenite phases against slip processes and improve thermomechanical behavior. Tensile properties, work behavior, and dimensional stability during repeated thermal cycling under load for the ternary and quaternary alloys were compared. The relative difference in yield strength between the martensite and austenite phases and the dimensional stability of the alloy were improved by the quaternary additions, while work output was only minimally impacted. The three alloys were also thermomechanically processed by cycling repeatedly through the transformation range under a constant stress. This so-called “training” process dramatically improved the dimensional stability in these samples and also recovered the slight decrease in work output caused by quaternary alloying. An added benefit of the solid-solution strengthening was maintenance of enhanced dimensional stability of the trained material to higher temperatures compared to the baseline alloy, providing a greater measure of over-temperature capability.

Introduction

Ever since the discovery of shape-memory behavior in NiTi, people have been vigorously exploring possible uses for this material. Applications that would otherwise require bulky hydraulic, pneumatic, or motorized actuators are beginning to look like possible candidates for shape-memory actuators, especially in space or weight constrained systems. Just in the aerospace, automotive, and power generation industries, there

are thousands of current and potential applications for shape-memory-based actuators or connectors. In many cases, such as aircraft engines, which basically operate in a single configuration optimized for a particular portion of the flight envelope, additional adaptive structures could be used to maximize the performance and efficiency of the engine over the entire mission. However, because space is extremely limited and weight is a valuable commodity, hydraulic and pneumatic actuators are not practical. But shape-memory actuators such as NiTi would be ideal due to their low weight, small volume, low power input, and high work output [1]. However, because these actuator systems operate at high temperature and binary NiTi has a transformation temperature range below about 100°C [2], alloys with higher transformation temperatures have to be developed for these types of applications.

It has been known for some time that alloying additions can be used to affect changes in the transformation behavior of NiTi alloys and that certain additions (e.g., Pd, Pt, Au, Hf and Zr at levels of greater than approximately 10at%) can be used to increase the transformation temperatures [3 -10]. However, the majority of the research performed on these high-temperature systems has been limited to studies of the transformation temperatures and products or focused on the shape-memory behavior (strain recovery under no-load conditions.) Very little effort has focused on necessary actuator type measurements such as work output and dimensional stability during thermal cycling under load. The notable exceptions are very recent work on NiTiHf thin films [11,12] and bulk NiTiPt [13] and NiTiPd [14,15] alloys.

In particular, Noebe et al. [13] determined the work output and tensile behavior of a series of bulk NiTiPt alloys having transformation temperatures over 240°C (A_s). In that investigation, an alloy containing 20at% Pt with excellent work behavior and dimensional stability was identified, providing the first glimpse into the performance of bulk high-temperature shape-memory materials. However, the high cost of platinum is a deterrent to using NiTiPt alloys and so NiTiPd has been evaluated as an alternative alloy system. A NiTiPd alloy with 30at% palladium was also evaluated by Noebe et al. [14] and exhibited comparable transformation temperatures and work output to that of Ni₃₀Ti₅₀Pt₂₀ [13]. However, work output in the Ni_{19.5}Ti_{50.5}Pd₃₀ alloy came at the

expense of significant permanent deformation per cycle, with more than 0.3% plastic strain at stresses above 100MPa [15].

For NiTiPd alloys to be effectively used as actuators with long cycle lives, this permanent deformation has to be significantly decreased or eliminated. A number of studies have focused on improving the shape-memory behavior of NiTiPd alloys through various mechanisms aimed at improving the alloys resistance to slip and thus promoting greater deformation by twin motion in hopes of enhancing the stress-free shape-memory behavior of these alloys. Such studies have involved the use of solid-solution strengthening [16,17], precipitate hardening [18], and various thermomechanical processing routines [19,20], with little success with the former and moderate success with the latter two approaches. These same processes are equally valid for improving the work output and dimensional stability of shape-memory alloys during thermal cycling under load. But none of these past studies [16-20] have addressed actuator type performance, and related issues. Therefore, the current investigation was conducted to determine the effects of solid-solution strengthening and thermomechanical processing on the work behavior and dimensional stability of a Ni_{19.5}Ti_{50.5}Pd₃₀ alloy.

Materials Processing and Characterization

Three alloys with target compositions of Ni_{19.5}Ti_{50.5}Pd₃₀, Ni_{19.5}Ti_{50.5}Pd₂₅Au₅, and Ni_{19.5}Ti_{50.5}Pd₂₅Pt₅ were produced by vacuum induction melting of high purity elemental constituents (99.98 Ni, 99.95 Ti, 99.995 Pd, 99.995 Pt, 99.995 Au) in a graphite crucible under an argon atmosphere at 20 torr. The furnace was equipped with tilt-pour capability, and each melt was cast into a copper mold to produce a 25.4 mm diameter by 102 mm long ingot with an appropriate hot top to accommodate shrinkage in the casting. All three ingots were homogenized at 1050°C for 72 hours and furnace cooled. The ingots were then vacuum sealed in mild steel cans and extruded into rods at 900°C utilizing an area reduction ratio of 7:1.

The extruded rods were cut into 50.8 mm long sections using wire electro-discharge machining (EDM). Using a computer numerically controlled (CNC) lathe, the cylindrical blanks were rough turned to remove the steel can and then threaded on each end with standard 3/8 inch – 24 UNF-2A threads. The samples were then turned to produce a final cylindrical gage

section 16.4 mm long by 3.81 mm in diameter. After machining, the cylindrical dog-bone-shaped samples were double wrapped in tantalum foil and heat treated at 400°C for 1 hour to relieve residual stresses in the material due to the extrusion and machining processes.

Compositional analysis of all three alloys was conducted using a Varian Vista Pro Inductively Coupled Plasma (ICP) Emission Spectrometer, a Leco TC-436 Nitrogen/Oxygen Determinator, and a Leco CS-444LS Carbon/Sulfur Determinator. Microstructural characterization of these materials was performed using a JEOL 840 SEM and Hitachi 4700 FE-SEM along with a Phillips CM-200 TEM.

Mechanical Testing Procedures

Monotonic Tensile Tests

Monotonic tensile testing was performed in an MTS-810 servo-hydraulic load frame with a digital controller able to control two digital channels simultaneously. Temperature was controlled by inductively heating both the sample gage and each of the threaded inserts holding the ends of the cylindrical dog-bone samples, to eliminate any temperature gradient across the sample. Temperature was measured using three type K thermocouples: one spot welded to the sample gage section and one spot welded to each of the threaded inserts. Samples were heated to the test temperature at a rate of 20°C/min and held isothermally for five minutes before testing was initiated. Straining of the samples was performed at a constant rate of $1 \times 10^{-4} \text{ sec}^{-1}$. Force was measured using a 100 kN load cell, and strain was measured using a high temperature extensometer with a range of -10/+20 percent.

Load-Bias Tests

Load-bias tests were performed by initially loading the sample in tension in the low temperature martensite state to produce a predetermined axial stress level in the gage. While the constant load was maintained, the samples were heated through the transformation range to the high temperature austenite state and then cooled again to the initial temperature. Successive loads were used to produce stresses of 0, 99, 197, 295, and 393 MPa. Two heat-cool thermal cycles were performed at each load level – the first to “reset” the material at that stress, and the second to measure behavior at that stress, for reasons discussed in detail in [13,14].

Table 1: Compositional analysis of three cast and extruded NiTiPdX alloys.

Extrusion (#) Sample ID	Density g/cm ³	Composition (atomic percent)							
		Ti	Ni	Pd	Au	Pt	C	N	O
Ext. 24 Ni _{19.5} Ti _{50.5} Pd ₃₀	7.504	49.6	19.5	30.2	0.0	0.0	0.44	0.017	0.26
Ext. 47 Ni _{19.5} Ti _{50.5} Pd ₂₅ Au ₅	7.983	49.6	19.4	25.2	5.0	0.0	0.39	0.014	0.25
Ext. 48 Ni _{19.5} Ti _{50.5} Pd ₂₅ Pt ₅	8.004	49.2	19.6	25.3	0.0	5.1	0.41	0.018	0.38

During each strain-temperature cycle, strain was measured as a function of temperature. Using this measurement, work output was calculated for the strain-temperature cycle at each stress level. For a shape memory alloy, work output is calculated as the integral of the applied stress with respect to the change in strain from the beginning to the end of the martensite-to-austenite transformation upon heating, which in a constant load situation simplifies to the applied stress times the transformation strain. The amount of plastic or permanent deformation that occurs during each strain-temperature cycle is a measure of the material's dimensional stability. It is calculated as the difference between the initial and final strains from the load-biased thermal heat-cool cycle. This plastic deformation is sometimes referred to in this paper as open-loop strain or ϵ_{OL} . A perfectly dimensionally stable material would have the same initial and final strain after a given heat-cool thermal cycle or $\epsilon_{OL} = 0$.

Thermomechanical Processing or “Training”

Thermomechanical processing, or “training”, involved thermally cycling the sample at zero load to “recover” the material to a consistent baseline condition, and then loading the sample to produce a stress of 345 MPa. The sample was held at this constant load and thermally cycled 10 times (unless indicated otherwise) through the transformation range of the alloy. After these training cycles, the sample was then unloaded and the effect of the thermomechanical processing evaluated by either thermally cycling the alloy repeatedly at 172 MPa or by performing a standardized incremental load-bias test on the sample, as described in the previous section.

Results & Discussion

Material Characterization

Table 1 contains the results of the compositional analyses of the three ingots. Within the resolution of the ICP analysis technique, the individual ingots were not discernibly different in composition from their respective aim compositions, with the possible exception of the $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Pt}_5$ alloy which appeared to be slightly lower in Ti. In addition, oxygen and carbon (due to the use of graphite crucibles) were present in essentially equal levels within all the extrusions. Density measurements, made as a part of a standard battery of characterization tests, showed an increase in bulk density due to substitution of gold and platinum for the lighter element palladium (Table 1).

The microstructures of the extruded and stress relieved alloys ($400^\circ\text{C}/1\text{h}$) are shown in Fig. 1. While the measured compositions (Table 1) for all three alloys indicated that the alloys were essentially stoichiometric e.g., $\text{Ti}:(\text{Ni}+\text{Pd}) = 1$ or even slightly $(\text{Ni}+\text{Pd})$ -rich in the case of the $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Pt}_5$ alloy, all three alloys exhibited microstructural features indicating that they were slightly Ti-rich in composition, consistent with their aim compositions.

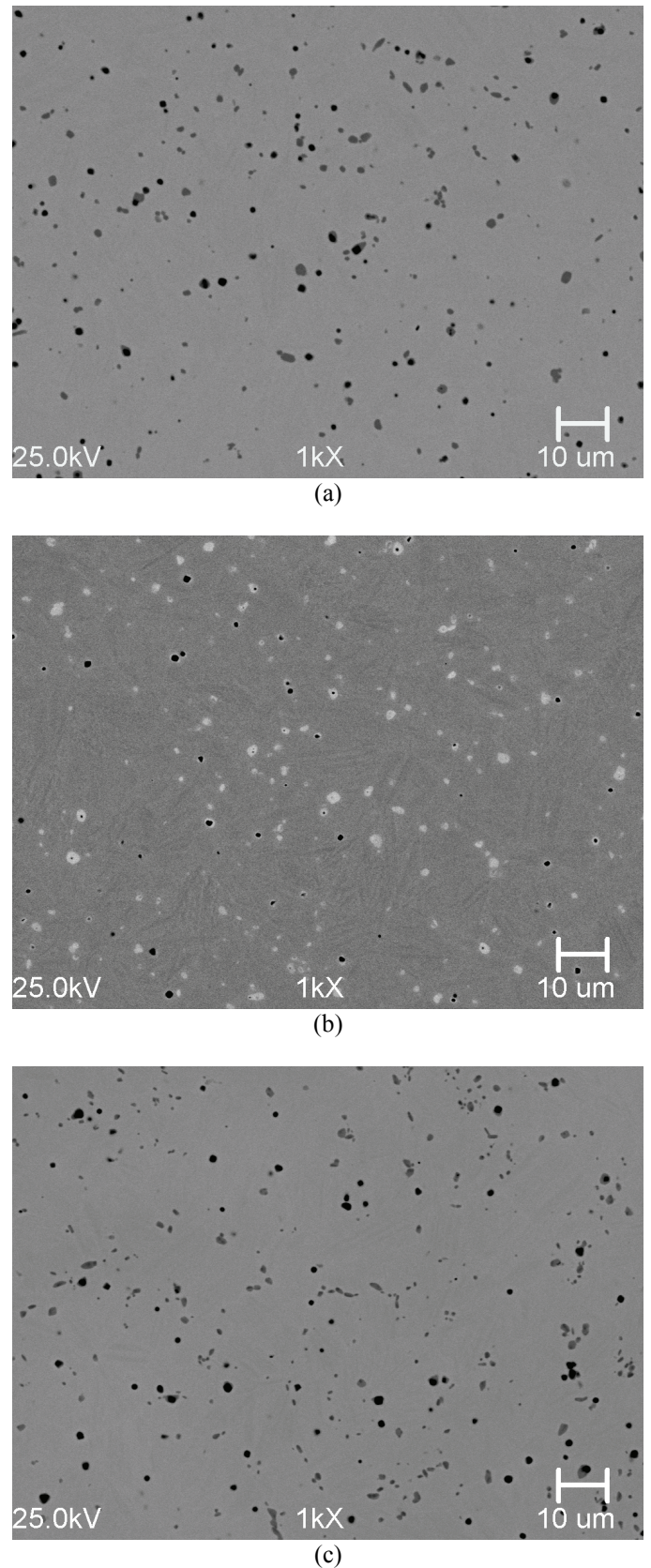


Figure 1: Basic microstructures of the a.) $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$, b.) $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Au}_5$, and c.) $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Pt}_5$ alloys.

The three alloys were martensitic at room temperature and predominantly single phase containing a small volume percent of second phase particles. A previous study [14] confirmed that the baseline alloy was a B19 orthorhombic martensite, typically observed in ternary alloys with greater than about 10at% Pd [4]. In all three alloys, there were two types of second phases present, an intermetallic phase containing Ti, Ni and X, (X: Pd, Pt, Au) and the other containing a high amount of Ti tied to the interstitials, C and O. Electron diffraction and energy dispersive spectroscopic (EDS) analysis indicated that the former phase was $Ti_2(Ni,X)$, which is isostructural to the face-centered-cubic Ti_2Ni phase commonly observed in Ti-rich NiTi alloys. The $Ti_2(Ni,Pd)$ phase had a lattice parameter $a_0 = 1.16$ nm. Ti_2Ni has a high solubility for interstitially located oxygen [21] and given the high oxygen content in these materials, the $Ti_2(Ni,Pd)$ probably contained some oxygen as well. The other phase was a typical fcc structured $Ti(C,O)$ with $a_0 = 0.44$ nm. Accommodation of these Ti-rich oxy-carbides while still trying to maintain a slightly Ti-rich stoichiometry to ensure a high transformation temperature [18] is the primary reason why the alloy was intentionally made rich in Ti from stoichiometry.

The average particle size of the $Ti_2(Ni,X)$ and $Ti(C,O)$ phases in all three alloys was ~ 1.0 μm and 1.4 μm , respectively and the total volume fraction of second phases was less than 4%. These results indicate that most of the quaternary alloying additions remained in solid solution in the matrix and did not significantly alter the basic microstructure of the quaternary alloys compared to the baseline alloy.

The transformation temperatures for the three alloys were determined via no-load load-bias testing, in the manner described previously in the “Mechanical Testing Procedures” section. The results are summarized in Table 2, and indicate that all three alloys exhibited essentially the same transformation temperatures suggesting that small amounts of Au and Pt substitutions for Pd in NiTiPd alloys do not alter the transformation temperatures.

Table 2: Transformation temperatures as determined via no-load load-bias testing.

Composition (at%)	Extrusion (#)	Transformation Temperature (°C)			
		M_F	M_S	A_S	A_F
$Ni_{19.5}Ti_{50.5}Pd_{30}$	24	233	249	250	259
$Ni_{19.5}Ti_{50.5}Pd_{25}Au_5$	47	226	243	239	257
$Ni_{19.5}Ti_{50.5}Pd_{25}Pt_5$	48	228	247	243	259

Quaternary Alloying Effects on Tensile Behavior

Tensile curves for the various alloys tested at $50^\circ C$ below the martensite finish temperature ($M_F - 50^\circ C$) and at $50^\circ C$ above the austenite finish temperature ($A_F + 50^\circ C$) are shown in Figs. 2a and 2b, respectively. These temperatures were chosen to represent the basic properties of the material in the martensite and austenite conditions, respectively. The yield strengths from these tests are plotted in Fig 3 along with the yield strengths of $Ni_{49.5-x}Ti_{50.5}Pd_x$ alloys of varying Pd contents [15].

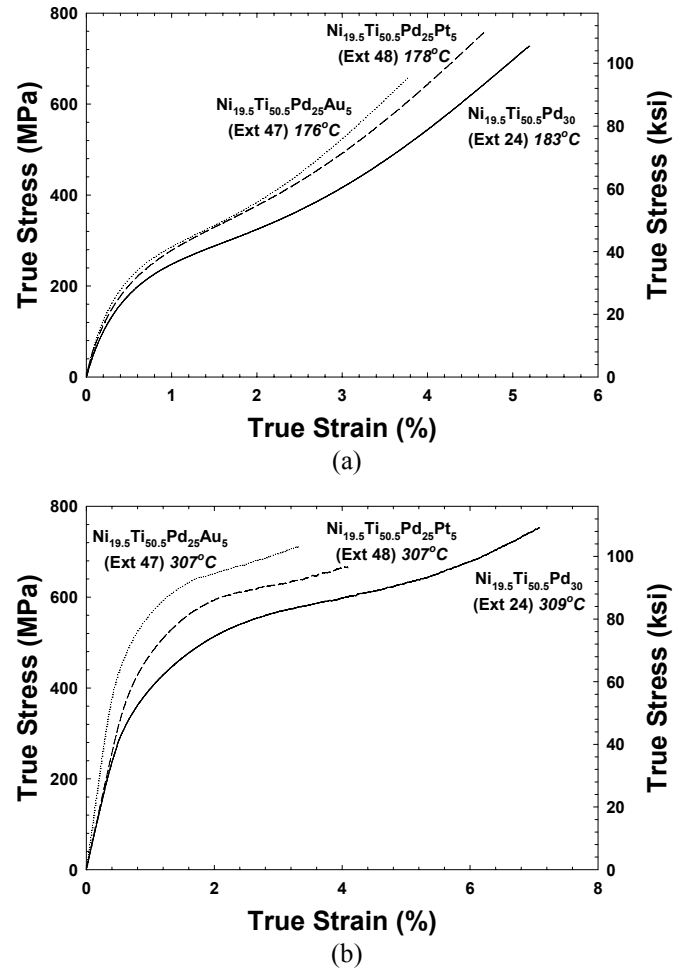


Figure 2: Representative tensile stress-strain curves for the various alloys tested in the a.) martensite condition ($M_F - 50^\circ C$) and b.) the austenite condition ($A_F + 50^\circ C$).

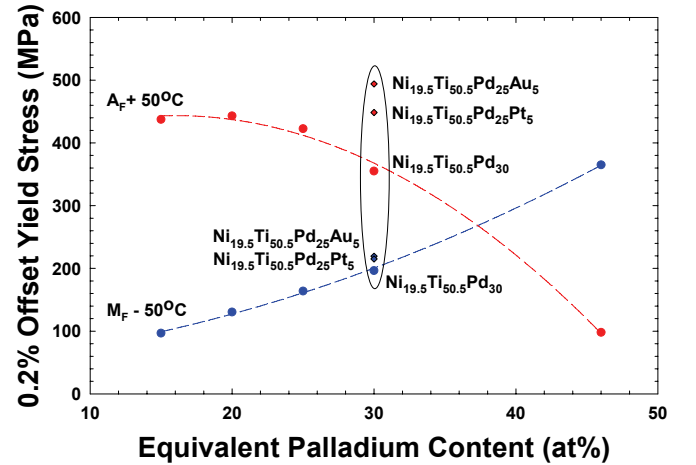


Figure 3: Improvement in relative yield strength by quaternary alloying $Ni_{19.5}Ti_{50.5}Pd_{30}$ with gold and platinum.

In the context of shape memory alloys, a good solid-solution strengthening agent is one that will raise the yield stress of the austenite phase while having only a marginal impact or preferably decreasing the yield stress of the martensite phase. In this way, the maximum difference in yield stresses between

the austenite and martensite is achieved. In the martensite state, the yield stress was increased with respect to the baseline alloy, but only minimally; by 23 MPa for 5at% Au substitution and 19 MPa for 5at% Pt substitution for Pd (Figs. 2a and 3). However, in the austenite state (Figs. 2b and 3), the quaternary alloys show an increase in the austenite strength of 139 MPa and 93 MPa, respectively. Therefore, the increase in relative yield stress due to the Au and Pt quaternary alloying additions is 116 and 74 MPa, respectively. This relative yield stress is the difference between the yield strength of the austenite phase, which corresponds to the critical stress for slip in the austenite, and the yield strength in the martensite phase, which corresponds to the martensite twin deformation stress. It is clear that both Au and Pt are successfully able to improve both the relative yield strengths (Fig. 3) and at the same time retain the high transformation temperatures of the baseline ternary $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$ alloy (Table 2).

Along with being used to determine basic material properties such as strength and ductility, tensile testing can be used as a first approximation to quickly determine the viable upper temperature limit or composition, at which a system would no longer be viable for actuator applications (see Fig. 3 and ref. [15]). It is obvious that as a minimum requirement, viable actuator materials (work producing with low plastic deformation) would need a positive relative yield stress. A strongly positive relative yield stress is necessary because when stress is applied to the material, deformation can occur via shear of the martensite twins at low temperatures and only elastic deformation of the austenite occurs when the material is cycled to higher temperature. Thus all deformation processes are recoverable. Conversely, viable work output is not possible in the reverse situation, when the yield strength of the martensite exceeds that of the austenite, since the stress necessary to cause deformation by detwinning will be greater than the yield stress of the austenite and the material will undergo significant plastic deformation with each thermal cycle. Of course this is just a minimum requirement as it does not take into account plastic deformation of the martensite phase due to dislocation processes, which also must be avoided to achieve good dimensional stability, as will be discussed below.

Quaternary Alloying Effects on Work-Related Properties

Each of the three alloys underwent load-bias testing to model their behavior as actuators. The stress-temperature response of the ternary $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$ alloy at different stress levels is shown in Fig. 4. The general behaviors for the $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Au}_5$ and $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Pt}_5$ alloys were similar but are omitted due to space limitations. Work output for all three alloys was good with the ternary alloy having a slightly larger work output for a given stress at the lower stress levels compared to the quaternary alloys (Fig. 5) due to a slightly larger transformation strain at these stress levels. However, the opposite was true at the highest stress levels, with the Au-containing alloy exhibiting the highest transformation strain at 295 and 393 MPa and therefore the highest work output at these stress levels. Overall, solid-solution strengthening provided no real advantage in terms of work output, except at

the highest stress levels, since the relative spread in yield strength between the martensite and austenite phases was sufficient to allow reasonable work output at most stress levels even in the ternary alloy. Judging from the trends in Fig. 3, solid solution strengthening would have a more significant effect on alloys containing higher Pd contents where the difference between the austenite and martensite strengths is much less.

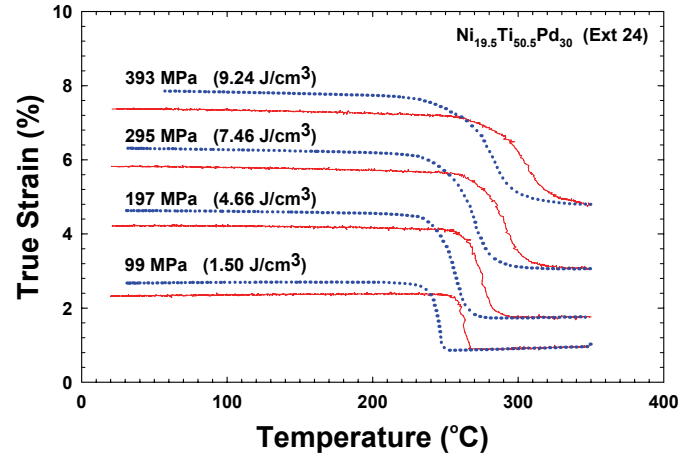


Figure 4: Strain-temperature response of the $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$ alloy at various stress levels. Solid lines are heating curves and dotted lines are cooling curves.

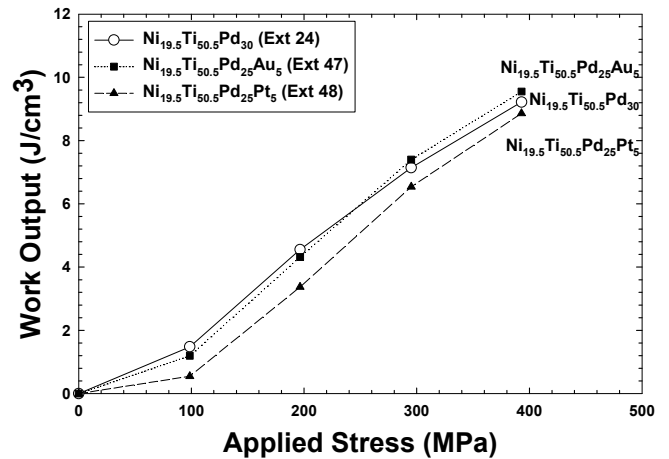


Figure 5: Work output for load-bias tested samples as a function of applied stress.

The open loop strains are plotted in Fig. 6 for all three alloys. At stresses up to 197 MPa, the plastic deformation per cycle in the quaternary alloys was only about one-half of that exhibited by the ternary alloy. This is seen as an advantage of solid-solution strengthening. However, the beneficial effect of Au was lost at the higher stress levels while a significant improvement was maintained at all stress levels for the Pt-containing alloy.

By examining Fig. 4, it is apparent that during each thermal cycle at a given stress level, the strain on cooling was greater than the strain on heating through the transformation range.

Therefore, the major contributing factor to the permanent deformation occurring per cycle was due to plastic deformation of the martensite phase. Consequently, the alloying additions, particularly Pt, must increase the resistance of the martensite phase to deformation by dislocation processes, thus increasing the dimensional stability of the alloy. However, significant improvements are still needed if these alloys are to be used in long-term cyclic applications.

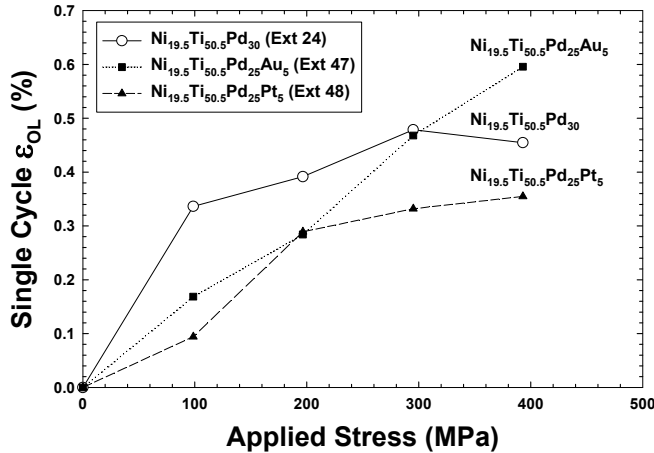


Figure 6: Permanent deformation in load-bias tested samples as a function of applied stress.

The Need for Thermomechanical Processing

From the results discussed in the previous section, it can be seen that while ternary NiTiPd alloys can be useful as high-temperature shape-memory alloys, they are also dimensionally unstable at essentially all stress levels when thermally cycled under constant stress. Therefore, they cannot be used in applications requiring dimensional stability over even a limited number of cycles. For instance, in an application where no more than 2% dimensional change in the actuator can be tolerated and working temperatures dictate the use of a high-temperature alloy like Ni_{19.5}Ti_{50.5}Pd₃₀, this strain would be reached in only six to seven cycles at 100 MPa. Solid-solution strengthening of these alloys can dramatically improve the per-cycle permanent deformation or open-loop strain at 100 MPa from 0.34% in Ni_{19.5}Ti_{50.5}Pd₃₀ to 0.17% in Ni_{19.5}Ti_{50.5}Pd₂₅Au₅ and 0.09% in Ni_{19.5}Ti_{50.5}Pd₂₅Pt₅, but only extends the useable cyclic life of an actuator made from these materials by a factor of two or three. Therefore, in order for these materials to be used over many cycles, it is absolutely necessary that methods be developed to strengthen and stabilize them against permanent deformation.

Golberg et al. [19] reported that thermomechanical treatment of a Ni₂₀Ti₅₀Pd₃₀ alloy by cold rolling and subsequent heat treatment successfully improved the no-load shape-memory behavior of the alloy compared to that of the baseline Ni₂₀Ti₅₀Pd₃₀ material reported by Shimizu et al. [18]. Recent research on Ti_{50.5}Ni_{29.5}Pt₂₀ HTSMA wires thermally cycled under load revealed a significant reduction in the subsequent amount of per-cycle permanent deformation when tested at a lower stress level [22]. These encouraging results form the basis of the training research performed, in an effort to better

quantify and understand the effects of thermomechanical processing alone and in conjunction with solid-solution strengthening on the work behavior and dimensional stability of this promising high-temperature shape memory alloy system.

Thermomechanical Processing Effects on Work-Related Properties

The thermomechanical processing that the alloys underwent consisted of cycling the samples through their transformation range ten times under a constant stress of 345 MPa to a high temperature of 350°C. The purpose of the training was to introduce a stable dislocation substructure in the materials that would hopefully strengthen the martensite phase against slip, resulting in increased dimensional stability, as well as to align the martensite variants in a manner that would optimize the transformation strain and thus the work output.

The result of this training on the cumulative open loop strains for all three alloys as a function of stress level after standard incremental load bias testing is shown in Fig. 7. For ease of comparison, Fig. 7 also contains the equivalent data for the same alloys in the untrained condition from Fig. 6. At all stress levels the trained materials showed a remarkable reduction in the amount of plastic deformation that was associated with each strain-temperature cycle. The open loop strains during load-bias testing of the trained materials were actually negative at 0 MPa and become positive but very close to zero at applied stresses of 99 MPa and 197 MPa, with values between 0.03% and 0.06% percent with the smallest values observed for the Ni_{19.5}Ti_{50.5}Pd₂₅Au₅. Very little plastic deformation occurred even at 393MPa, which is greater than the 345MPa training stress, with open loop strains of 0.19, 0.18, and 0.13%, for the Ni_{19.5}Ti_{50.5}Pd₃₀, Ni_{19.5}Ti_{50.5}Pd₂₅Au₅, and Ni_{19.5}Ti_{50.5}Pd₂₅Pt₅ alloys, respectively. These strains are much lower than the corresponding open loop strains of 0.46, 0.67, and 0.36% in the untrained samples at this stress level.

It is interesting to note that the open loop strain determined at the start of the load-bias tests under essentially zero stress was actually negative. This meant that the sample was shorter at the end of the cycle compared to its starting length. This phenomenon is quite common after training and is thought to occur for two reasons: (1) residual internal stresses in the material produced by cycling under high load are greater than those that would be imposed by a lesser or no load on the sample after training, and (2) the amount of martensite variants preferentially oriented by the training stress is greater than the amount thermodynamically preferred at the lower stress. While all of the initial preferentially oriented variants are acting to produce strain during the heating cycle, some of these variants revert to a self accommodating mode upon cooling, and so the transformation strain upon cooling could be less than that during heating. Thus, as the sample is heated, and then cooled, these two processes result in a net decrease in strain over one whole cycle, which translates into a negative open loop strain.

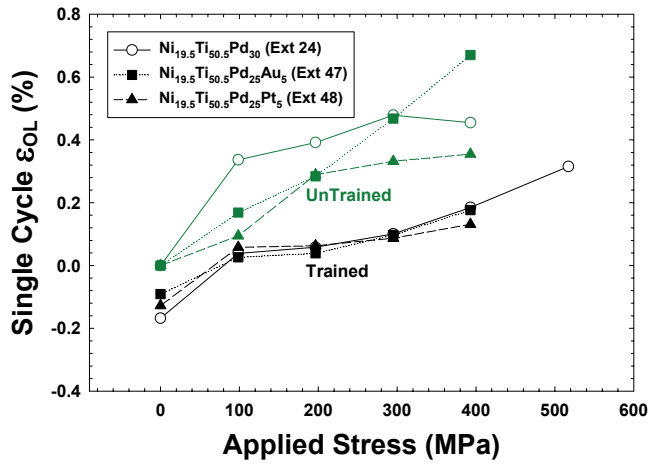


Figure 7: Effect of thermomechanical processing on permanent deformation(open loop strain) for samples trained and subsequently load-bias tested.

While training proved to be successful in significantly increasing the dimensional stability of all the alloys by reducing the amount of permanent deformation, the transformation strains of the trained samples were not found to be significantly greater than those for the untrained samples, except for slight improvement at 0 and 99 MPa. However, training does produce an interesting plateau effect regarding transformation strains. When the samples are trained, self accommodating martensite twin variants are reoriented such that the strain produced during transformation to and from austenite acts along the tensile axis. The plateau effect is representative of equivalent amounts of variants being oriented in the preferred direction producing equivalent transformation strains at a variety of stress levels. While this plateau effect means that work output is slightly improved at 99MPa over that for untrained samples, it also results in all three alloys producing equivalent amounts of work at each stress level up to 393MPa after training, as shown in Fig. 8.

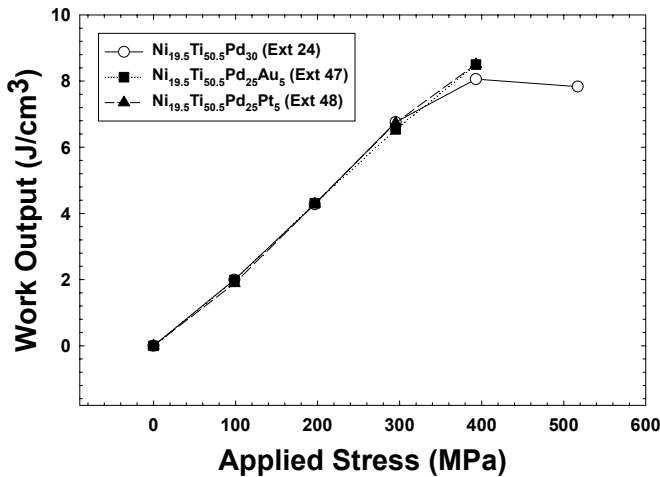


Figure 8: Work output as a function of applied stress after thermomechanical processing.

Effect of Thermomechanical Training on Dimensional Stability of Thermally Cycled Samples

Given the dramatic improvements in dimensional stability during individual thermal cycles due to the particular training regime instituted in this study, the effect of training on the cyclic behavior was further investigated for all three alloys. Consequently, after training, each alloy was thermally cycled repeatedly at 172 MPa (25 ksi), which is a reasonable stress an SMA actuator would be expected to handle under very long life conditions (> 100,000 cycles). The cumulative strains for all 10 post-training cycles are plotted in Fig. 9, and those for the untrained, 1st and 10th cycle are summarized in Table 3. It is clear from these results that the amount of plastic deformation after cycling under 172 MPa was less in the quaternary alloys after 1 and 10 cycles compared to the baseline alloy. The average ϵ_{OL} after 10 cycles at 172MPa was 0.0039, 0.0012, and -0.0019% respectively for the baseline, gold-alloyed, and platinum-alloyed materials. This difference in ϵ_{OL} suggests that training, although successful in improving the dimensional stability of all three alloys, is more effective in Au and Pt containing solid-solution strengthened alloys than in the baseline.

Table 3: Training effects on the open loop strain in samples thermally cycled at 172MPa.

Composition (at%)	Cumulative ϵ_{OL} (%)		
	Untrained	1 st Post Training Cycle	10 th Post Training Cycle
Ni _{19.5} Ti _{50.5} Pd ₃₀	0.42	-0.0025	0.039
Ni _{19.5} Ti _{50.5} Pd ₂₅ Au ₅	0.29	-0.0016	0.012
Ni _{19.5} Ti _{50.5} Pd ₂₅ Pt ₅	0.32	-0.0054	-0.019

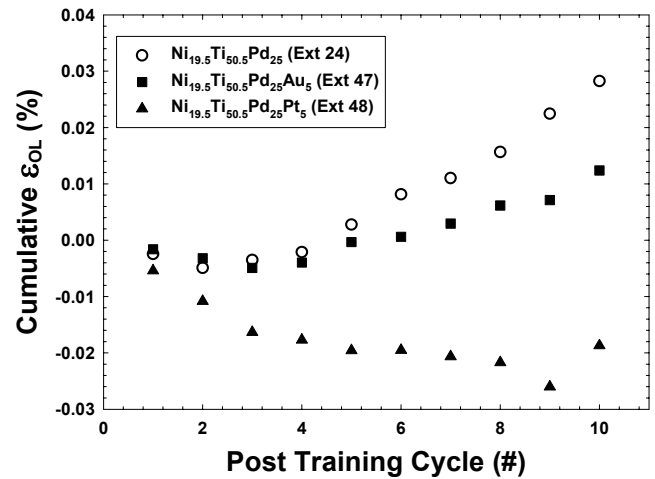


Figure 9: Cumulative plastic deformation after training.

Temperature Limits and Thermal Stability of NiTiPdX Alloys

There are two main modes of operation of a shape memory alloy as an actuator: differential strain control or on/off actuation. In differential strain control, temperature and/or current in the material are closely controlled, allowing the user to partially transform the material. However, this method of operation is complicated, and extensive control algorithms are

necessary along with extensive characterization of the material's strain-temperature response under various loading conditions. Therefore, many applications rely on on/off type actuation where the material is either fully strained in the martensitic state or fully recovered and in the austenite state, and hard stops are used to limit strain if needed. Temperature is often not of great concern to the user and the only requirement is that the SMA be either above the A_F or below the M_F . However, this oversimplification can lead to overheating of the shape memory alloy and serious degradation in performance.

To illustrate this point, two $Ni_{19.5}Ti_{50.5}Pd_{30}$ samples with $A_F = 259^\circ C$ were trained to optimize dimensional stability as described previously and then thermally cycled under a load of 345 MPa. However, one sample was only cycled to a high temperature of $350^\circ C$, while the other was cycled to $450^\circ C$; both samples were cooled to below $100^\circ C$. The resulting load-bias curves are shown in Fig. 10. The sample cycled to a higher temperature of $450^\circ C$ shows significant evidence of creep, as indicated by a rounding of the strain-temperature heating curve at temperatures above the transformation, resulting in a significant amount of plastic deformation during the cycle. In this case, the large amount of plastic deformation during the thermal cycle is predominantly due to creep deformation of the austenite phase. The sample cycled to $350^\circ C$ did not have a chance to creep and thus the total plastic deformation during the thermal cycle was extremely low and due predominantly to slip processes in the martensite phase as discussed in the previous sections. It should be noted that all load-bias testing and training discussed previously in this paper for all three alloys involved thermal cycling to a maximum temperature of $350^\circ C$.

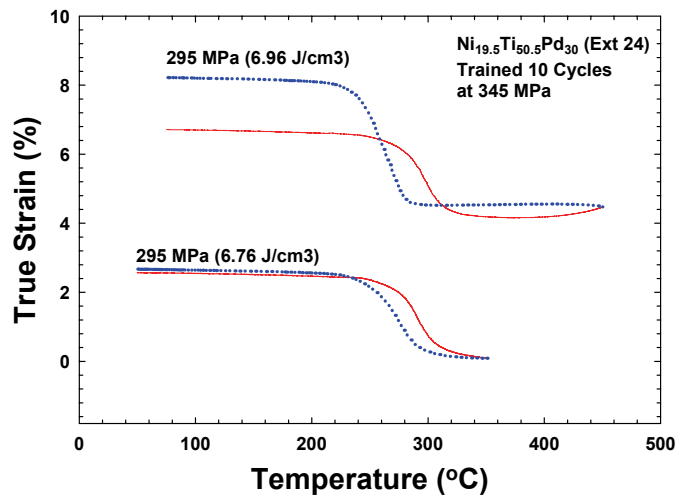


Figure 10: Effect of upper temperature on the cyclic behavior of a $Ni_{19.5}Ti_{50.5}Pd_{30}$ alloy thermally cycled under constant load. Solid lines are heating curves and dotted lines are cooling curves.

At temperatures where creep begins to occur, there is not only direct damage to the shape memory alloy due to creep processes, but there are also other more subtle problems that can occur due to overheating. These include recovery or even

recrystallization of the microstructure, which may undo the microstructure developed intentionally in the material to improve such things as dimensional stability. Therefore, in addition to characterizing the basic mechanical properties and work related behaviors (such as work output, transformation strain, and dimensional stability) it is also necessary to characterize the thermal stability of the material to determine the highest safe operating temperature that can be reached without leading to a degradation in other properties. This way, a type of thermal safety limit can be determined for the material, which will then tell an applications engineer or end user how careful they must be when utilizing a particular shape memory alloy. Obviously the greater the difference between the austenite finish temperature and this upper temperature limit, the greater the margin of safety the material will have for over temperature conditions.

To show that long term dimensional stability could be maintained for a long period of time when cycled to a high temperature of $350^\circ C$, a sample of the baseline alloy was specially trained a total of 20 times (instead of 10 times) at 345MPa and cycled thereafter at 172MPa for a total of 140 cycles. In the first couple of cycles, the sample exhibited negative open loop strain. Afterwards, the open loop strain became positive and in the last 110 cycles it was stable with a cumulative ϵ_{OL} of 0.163%, which translates to an average ϵ_{OL} of $1.48E-3$ % per cycle.

In order to determine this upper temperature limit for shape memory alloys, a special load bias test was developed. During this test an alloy is trained for 10 cycles at 345MPa and then thermally cycled repeatedly under a reduced load equivalent to 172MPa. However, during the course of the test the upper temperature that the sample is cycled to is slowly incremented by $10^\circ C$ after every 10 complete cycles. The advantage of doing this is that the cumulative plastic deformation for the sample can be essentially determined as a function of temperature.

This test was first applied to the baseline $Ni_{19.5}Ti_{50.5}Pd_{30}$ alloy. To ensure that the starting material was optimized for dimensional stability, it was thermomechanically processed or trained as previously described by thermally cycling through the transformation range for 10 cycles under a stress of 345 MPa. As discussed earlier, the trained material is dimensionally stable when thermally cycled between $50^\circ C$ and $350^\circ C$ resulting in a cumulative strain of only 0.163% after 110 cycles. This trained material was then subjected to our modified load-bias test to determine the effect of increasing temperature above the A_F on dimensional stability.

As seen in Fig. 11, while the sample cycled to a maximum of $350^\circ C$ remained stable over all 110 cycles, with a cumulative ϵ_{OL} of 0.1633%, the sample cycled at incrementing higher temperatures developed high levels of permanent deformation which were affected more strongly by the increasing temperatures and resulted in 6.47% cumulative ϵ_{OL} .

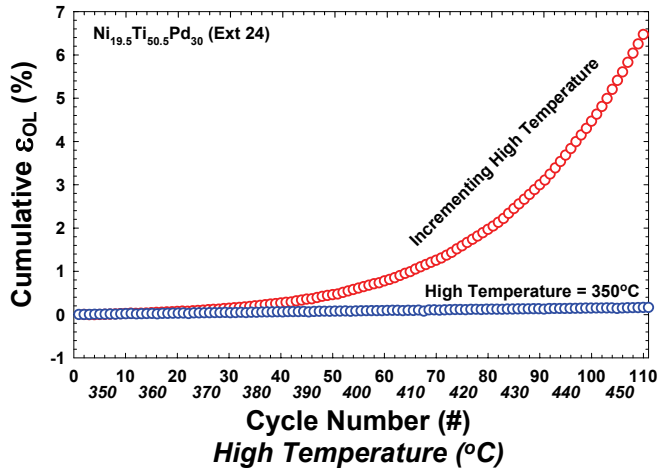


Figure 11: Effect of increasing high temperature limit on the stability of the baseline $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$ alloy.

During thermal stability testing of the trained samples, the $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Pt}_5$ alloy of extrusion 48 failed on the 97th cycle of the thermal stability part of the test, and another sample had to be tested (the sample had accumulated a total of 1.5% strain over the 97 thermal stability cycles and a maximum total strain of 6.5% including that due to recovery, training, and thermal stability cycles). Even this failure provided useful results, as all the data points for the two tests on that composition match until six cycles before failure, showing the repeatability of the test and the extent to which the influence of crack growth on the open loop strain can be isolated.

Over the course of the 110 thermal stability cycles, the two quaternary $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Au}_5$ and $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Pt}_5$ alloys accumulated only 1.99% and 1.54% permanent strain respectively, each of which is less than one-third of the permanent strain accumulated by the baseline $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$ alloy over the same number of cycles (Fig. 12). In order to isolate individual temperatures and quantify the effect on permanent deformation, the data from the 110 cycles was split up into separate bins relating to the high temperature reached during those cycles and the strain re-zeroed for the first cycle in each bin as shown in Fig 13. In this way, only the strain accumulated in each temperature range was accounted for. From this data, it can be seen that softening of the $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$ alloy really begins to take affect around 390-400°C, which correlates well with the data from Xu et al. [23], in which a large decrease in hardness is seen centered around 400°C. In comparison, the quaternary alloys show an improvement in high temperature thermal stability due to Pt and Au solid-solution strengthening and begin to be largely affected by softening at 420-430°C, an increase of 30°C over the baseline ternary alloy.

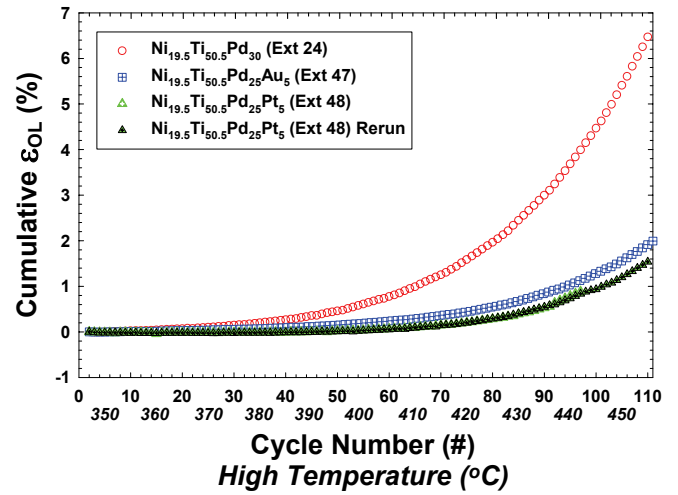


Figure 12: Effect of increasing high temperature limits on the cyclic stability of the three NiTiPdX alloys.

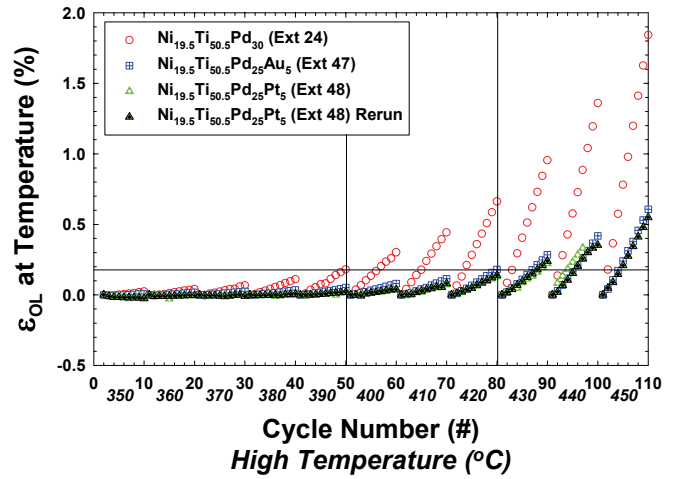


Figure 13: Same data as Fig. 12, but showing the individual temperature effects on the dimensional stability of alloys cycled to specific high temperatures.

Conclusions

From this research, it is concluded that the quaternary substitution of 5.0 at.% of Au or Pt for Pd in $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$ alloys can improve the permanent deformation behavior of these high-temperature shape-memory alloys. However, training has a stronger effect than quaternary alloying, and alone can increase the dimensional stability of NiTiPd alloys. Training can also effectively produce equal work output and permanent deformation behavior in ternary $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$ alloys and quaternary $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Au}_5$ and $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{25}\text{Pt}_5$ solid-solution strengthened alloys. Nevertheless, quaternary alloying is still helpful since it provides the additional benefit of increased thermal stability by as much as 30°C over the ternary $\text{Ni}_{19.5}\text{Ti}_{50.5}\text{Pd}_{30}$, which in turn leads to a greater safety factor against overheating.

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